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SALES hereby certify that annexed is a true copy of the Provisional specification  
in connection with Application No. 2003901788 for a patent by  
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
ORGANISATION as filed on 15 April 2003.



WITNESS my hand this  
Twenty-third day of April 2004

LEANNE MYNOTT  
MANAGER EXAMINATION SUPPORT  
AND SALES

**AUSTRALIA**

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***Patents Act 1990***

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# **PROVISIONAL SPECIFICATION**

**Invention Title:            Production of layered double hydroxides**

**The invention is described in the following statement:**

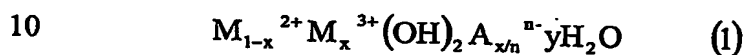
## PRODUCTION OF LAYERED DOUBLE HYDROXIDES

### Field of the invention

The present invention relates to methods for producing layered double hydroxide compounds. The present invention is particularly suitable for producing hydrotalcites, especially hydrotalcite in which the interlayer anion is nitrate.

### Background of the invention

Layered double hydroxides (hereinafter referred to as "LDH compounds") are mixed hydroxides of divalent and tri-valent metals having an excess of positive charge that is balanced by interlayer anions. They can be represented by the general formula (1).



where  $M^{2+}$  and  $M^{3+}$  are di- and tri-valent metal ions respectively and  $A^{n-}$  is the interlayer anion of valance n. The x value represents the proportion of trivalent metal to the total amount of metal ion present and y denotes variable amounts of interlayer water.

Common forms of LDH comprise  $Mg^{2+}$  and  $Al^{3+}$  (known as hydrotalcites) and  $Mg^{2+}$  and  $Fe^{3+}$  (known as pyroaurites), but other cations including Ni, Zn, Mn, Ca, Cr, and La are known. The amount of surface positive charge generated is dependent upon the mole ratio of the metal ions in the lattice structure, and the conditions of preparation as they affect crystal formation. LDH compounds are well known in industry, being used as catalysts in organic conversion reaction, PVC stabilisers, flame retardants, medicinal antacids, and in wastewater treatment.

In our co-pending International Patent Application No. PCT/AU01/00026, filed 12 January 2001, the use of LDH's in soil ameliorates and slow release fertilisers is described. The entire contents of International patent application no. PCT/AU01/00026 are incorporated herein by cross-reference.

In order to produce a fertiliser incorporating LDH's in accordance with the teachings of International patent application no. PCT/AU01/00026, the LDH's are contacted with one or more nutrient anions, such as nitrate, phosphate, sulphate and/or silicates. This results in the nutrient anions undergoing ion exchange with the interlayer

ions of the LDH's and the nutrient anions are "taken up" by the LDH's. Subsequent use of the thus-loaded LDH's can see the nutrient anions being re-exchanged after the thus-loaded LDH's are supplied to the soil to thereby supply the nutrient anions to the soil.

### Summary of the invention

5 In a first aspect, the present invention provides a method for producing a layered double hydroxide compound ("LDH") comprising mixing a nitrate containing a first metal with an hydroxide or a nitrate containing a second metal and ammonium hydroxide to produce the LDH and ammonium nitrate, wherein the LDH has nitrate ions as interlayer ions, and recovering the LDH and ammonium nitrate.

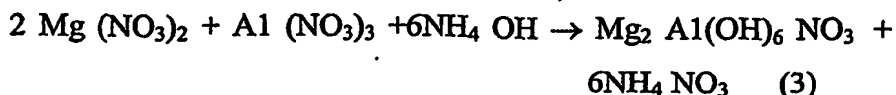
10 Preferably, the LDH material is hydrotalcite in which the first metal is magnesium and the second metal is aluminium. In this embodiment, it is especially preferred that magnesium nitrate is mixed with a nitrate or hydroxide containing aluminium and ammonium hydroxide to form hydrotalcite having nitrate as an interlayer anion and ammonium nitrate. The nitrate or hydroxide is preferable aluminium nitrate or sodium  
15 aluminate ( $\text{Na Al}(\text{OH})_4$ ).

Even more preferably, the method produces hydrotalcite by one of two possible paths:

- (a) mixing magnesium nitrate with sodium aluminate and ammonium hydroxide to form hydrotalcite having nitrate as an interlayer anion, ammonium nitrate and sodium nitrate, as shown in Formula (2):



- (b) Mixing magnesium nitrate with aluminium nitrate and ammonium hydroxide to form hydrotalcite having nitrate as an interlayer ion and ammonium nitrate, or shown in Formula (3).



The above synthesis routes are particularly preferred because they result in the production of a hydrotalcite having nitrates as interlayer anions. This product may be used directly as a fertiliser because the nitrate ion can be transferred to the soil when the hydrotalcite is mixed with soil, thereby supplying a nutrient anion to the soil. The hydrotalcite containing nitrate as an interlayer anion can also be ion exchanged such that phosphate and/or sulphate anions become interlayer anions if it is desired to transfer one or both of those anions to the soil. Such ion exchange can be suitably achieved, for example, by contacting the hydrotalcite containing nitrate as an interlayer anion with a solution containing ammonium phosphate and/or ammonium sulphate. It will also be understood that the LDH product may be used in a number of other applications and that it should not be considered to be limited to use as a fertiliser.

As a further advantage of the preferred embodiments of the first aspect of the present invention, ammonium nitrate is also produced. Ammonium nitrate can be used in the manufacture of explosives and fertilisers and is a potentially valuable product. In some embodiments, other valuable by-products may also be produced, such as sodium nitrate when the reaction as given in formula (2) takes place.

In the second aspect, the present invention provides a method for the manufacture of ammonium nitrate and LDH containing nitrate as an interlayer anion, the method comprising the steps of:

- (1) providing a source of nitric acid
- (2) providing a source of ammonia;
- (3) reacting ammonia with nitric acid to produce ammonium nitrate;
- (4) preparing a nitrate containing a first metal by reacting a compound containing the first metal with nitric acid or ammonium nitrate;
- (5) either:
  - (a) preparing a nitrate containing a second metal by:
    - (i) contacting a compound containing the second metal with nitric acid; or

- (ii) contacting a compound containing the second metal with ammonium nitrate; or
- (b) providing an hydroxide containing the second metal;
- (6) mixing the nitrate containing the first metal from step (4) with the nitrate containing the second metal or the hydroxide containing the second metal from step (5) and ammonium hydroxide to form the LDH containing nitrate as an interlayer anion and ammonium nitrate.

Preferably, the process further comprises:

- (7) recovering the LDH and the ammonium nitrate from step (6).

In one embodiment, the source of nitric acid may comprise a nitric acid plant. Alternatively, the source of nitric acid may be a nitric acid storage facility.

The source of ammonia is preferably an ammonium plant for the production of ammonia. The ammonia plant is suitably a plant for producing ammonia using the Haber process.

In one embodiment of the second aspect of the present invention, the source of nitric acid and the source of ammonia are components of a plant for producing ammonium nitrate. Ammonium nitrate is widely used in the production of fertilisers and explosives. As such, annual production worldwide of ammonium nitrate is large, with a commensurate abundance of ammonium nitrate plants. The method of this embodiment of the second aspect of present invention is preferably embodied as an addition to, or a retrofit to, an existing ammonium nitrate plant. By embodying the method of the second aspect of the invention in this way, it is possible to utilise ammonia and nitric acid used or manufactured in the ammonium nitrate plant as feed materials for the part of the plant that produces the LDH's.

With these comments in mind, it is apparent that steps (1), (2) and (3) of a preferred embodiment of the second aspect of the invention may comprise the process steps of an existing ammonium nitrate plant. The source of nitric acid may comprise a storage facility for storing nitric acid produced off-site or it may comprise a nitric acid production plant for producing nitric acid from suitable starting materials. Similarly, the

source of ammonia may be an ammonium storage facility for storing ammonia produced off-site or it may comprise an ammonia plant for producing ammonia from suitable starting materials.

5 Step (3) may comprise any suitable method for producing ammonium nitrate by reacting ammonia and nitric acid. Such methods are well known to those of skill in the art and need not be described further.

Step (4) requires that a nitrate containing a first metal be prepared. The first metal is preferably magnesium. If the second metal is aluminium, the LDH that is formed is hydrotalcite containing nitrate as interlayer anions.

10 The step of forming a nitrate containing magnesium may involve contacting a magnesium compound with nitric acid to form a nitrate containing magnesium. The magnesium compound may be magnesite ( $\text{MgCO}_3$ ), a readily-available inexpensive compound. Magnesium oxide ( $\text{MgO}$ ) may also be used, with calcined magnesia being suitable.

15 It will be understood that the term "a nitrate containing a first metal" encompasses a nitrate that may be in the form of a solid or in dissolved or melted form, in which case the nitrate compound is in a dissociated form. Preferably, the nitrate containing a first metal is in the form of an aqueous solution.

20 Step (5) of the method of the second aspect of the invention may comprise (a) reacting a compound containing a second metal with nitric acid or ammonium nitrate to form a nitrate of the second metal or (b) providing an hydroxide containing the second metal. The second metal is preferably aluminium.

25 Step (5)(b) may preferably comprise supplying sodium aluminate ( $\text{Na Al(OH)}_4$ ). The sodium aluminate may be supplied as part of a pregnant Bayer liquid from a bauxite digestion plant.

It will be appreciated that the nitrate containing the second metal may be in the form of a solid or in a dissolved or melted state, in which case the nitrate compound will be in a dissociated form. Preferably, the nitrate containing the second metal is in the form of an aqueous solution.

The hydroxide containing the second metal may also contain one or more other metals. It may also be in solid form, a dissolved state or a molten state. Preferably, it is in the form of an aqueous solution.

Step (6) of the method of the second aspect involves a reaction to form the LDH containing nitrate as the interlayer anion. The LDH thus formed is preferably hydrotalcite. The reaction preferably occurs by mixing aqueous solutions containing the first metal and the second metal under vigorous stirring whilst adding ammonium hydroxide at a rate sufficient to maintain the pH at about 9.5. Alternatively, the aqueous solutions containing the first metal and the second metal can be mixed in appropriate portions and then added to an ammonium hydroxide solution until the pH falls to about 9.5. The reaction may take place at ambient temperature and atmospheric pressure. Upon mixing, the LDH immediately forms. If a more crystalline product, or a product having larger particle size, is desired, the resulting slurry can be "aged" by, for example, holding at elevated temperature, eg at 80°C for 8 hours, or the slurry can be hydrothermally treated at elevated temperature and pressure.

In addition to producing LDH's, ammonium nitrate is also formed in step (5). When the method of the second aspect of the invention forms part of an ammonium nitrate plant, the "by-product" ammonium nitrate from step (vi) can be recovered as a valuable product for sale to consumers. This, of course, improves the economics of the process.

In another embodiment, the process of the second aspect of the present invention preferably comprises preparing the nitrate containing the first metal in step (4) by reacting the compound containing the first metal with ammonium nitrate. In this embodiment, the process may comprise the further step of:

- (8) recycling the ammonium nitrate from step (6) to step (4).

The ammonium nitrate that is recycled from step (6) to step (4) may pass to an intermediate storage before being recycled to step (4).

Preferably, step (4) comprises the step of reacting a compound containing the first metal with ammonium nitrate to form the nitrate containing the first metal and ammonia and the ammonia from step (4) is recycled to step (2) or step (3). Where the ammonia



from step (4) is recycled to step (2), the process may suitably comprise passing the ammonia to an ammonia storage facility, such as an ammonia tank.

In addition to producing LDH's, ammonium nitrate is also formed in step (6). In another embodiment, this ammonium nitrate can then be reacted with additional first metal compound (e.g. MgO) in step (4) to produce more first metal nitrate for LDH production. Preferably, ammonia is also produced in step (4), and this can be recycled for LDH production in step (6). This, of course, improves the economics of the process. Alternatively, the ammonia produced in step (4) can be recycled to the source of ammonia.

Nitrogen balances in this embodiment of the process of the present invention are such that if all of the ammonium nitrate produced in step (6) is reacted with sufficient first metal compound (e.g. MgO), the amount of first metal nitrate produced is in excess of that required for LDH production. As will be explained in the detailed description below, the excess first metal nitrate can be temporarily stored, and then used in step (6) during which time the reaction between ammonium nitrate and first metal compound (step (4)) is halted. This in turn leads to an accumulation of ammonium nitrate from step (6) which is subsequently used when normal operations are resumed. Thus a two stage-process involving the alternate storage of first metal nitrate and ammonium nitrate is envisaged.

In another embodiment of the present invention, step (5) may involve producing a nitrate containing the second metal by contacting a compound containing the second metal with ammonium nitrate. This allows the possibility of using some of the ammonium nitrate produced in step (6) to be returned to step (5). Indeed, in this embodiment, the ammonium nitrate produced in step (6) may be returned to step (4) or to step (5) (ie step (5)(a)(ii)), or, more preferably, to both step (4) and step (5). In this way, all of the ammonium nitrate produced in step (6) would be returned to the process and an amount of additional ammonium nitrate (from step (3)) would also have to be added to one or both of step (4) and step (5). The process of this embodiment does not produce excess ammonium nitrate and thus the process does not necessarily have to be appended to an ammonium nitrate plant. The process of this embodiment actually requires a net

input of ammonium nitrate, albeit at a reduced level, and thus the economics of the process are not dependent upon finding suitable markets for excess ammonium nitrate or being attached to an existing ammonium nitrate plant. Indeed, steps (1) to (3) of the process of this embodiment may take place at a location away from the site of steps (4) to (6), with steps (1) to (3) being equivalent to providing a source of ammonium nitrate to the site of process steps (4) to (6).

Thus, in the process of this embodiment, the process of the second aspect of the invention further comprises:

- (9) returning the ammonium nitrate produced in step (6) to one or both of steps (4) and (5). Preferably, the ammonium nitrate produced in step (6) is returned to step (4) and step (5).

In this embodiment, step (5) comprises step (5)(a)(ii). Suitably, the compound containing the second metal is  $Al(OH)_3$ .

The recovered LDH containing nitrate as an interlayer anion may be used as a slow release fertiliser in accordance with the teachings of an co-pending International patent application no. PCT/AU01/00026. It may also be ion-exchanged with sulphate and/or phosphate ions. This may produce a fertiliser for supplying sulphate and/or phosphate to the soil. This is preferably achieved by providing sulphuric acid and/or phosphoric acid and contacting with ammonia to make ammonium sulphate and/or ammonium phosphate. The ammonium sulphate and/or ammonium phosphate is then contacted with the LDH to exchange the nitrate interlayer anions. The by-product is ammonium nitrate. The LDH may also be used in other applications. For example, it could be used in the treatment of phosphatic wastes, such as chicken manure from chicken batteries.

## **Brief description of the drawings**

Preferred embodiments of the present invention will now be described with reference to the accompanying drawings in which:

Figure 1 shows a process flow sheet of one embodiment of a process in accordance with the present invention:

Figure 2 shows a process flow sheet of another embodiment of a process in accordance with the present invention;

Figure 3 shows a modified version of the process shown in Figure 2;

5 Figure 4 shows a process flow sheet of a further embodiment of a process in accordance with the present invention:

Figure 5 shows a process flow sheet of another embodiment of a process in accordance with the present invention;

Figure 6 shows a process flow sheet of a particular aspect of the process of Figures 4 or 5 in accordance with the present invention; and

10 Figure 7 is a flowsheet of a process in accordance with a further embodiment of the invention.

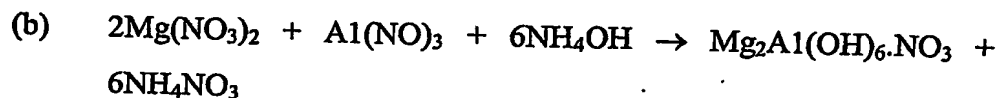
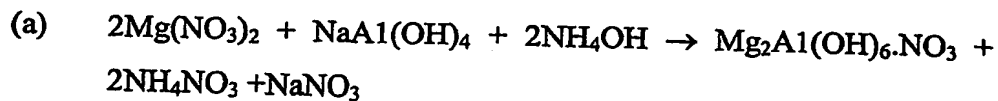
It will be understood that the following description of the preferred embodiments are provided to illustrate the invention and that the invention should not be considered to be limited to the embodiments described.

15 **Detailed description of the embodiments**

20 The schematic process flow sheets shown in figures 1 to 3 relate to the manufacture of hydrotalcite or layered double hydroxide compounds, particularly for use as slow release fertiliser materials. In particular, in the embodiments shown in figures 1 to 3, hydrotalcite-like compounds that contain nitrate, phosphate or sulphate in the interlayer spaces are produced by directly synthesising hydrotalcite containing nitrate as the interlayer anion ( $\text{NO}_3\text{-HT}$ ) and subsequently converting a portion of  $\text{NO}_3\text{-HT}$  into hydrotalcite containing phosphate as the interlayer anion ( $\text{PO}_4\text{-HT}$ ) and hydrotalcite containing sulphate as an interlayer anion ( $\text{SO}_4\text{-HT}$ ). Furthermore, any anion that can be exchanged with nitrate, such as silicate or borate, can be substituted into the interlayer spaces by ion exchange.

25

Two alternate synthesis pathways are proposed for the direct synthesis of  $\text{NO}_3\text{-HT}$ :



5        Either of these synthesis routes could be incorporated into an ammonium nitrate manufacturing plant, with the residue or by-product from the hydrotalcite plant (ammonium nitrate) rejoining the primary production stream.

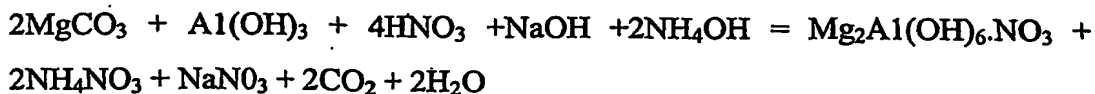
10        Figure 1 shows a schematic process flow sheet that illustrates the incorporation of pathway (a) into an ammonium nitrate plant. In figure 1, a conventional ammonium nitrate plant includes a nitric acid plant 10 and an ammonia plant 12. Nitric acid from nitric acid plant 10 and ammonia from ammonia plant 12 are mixed and reacted in reactor 14 to produce ammonium nitrate. Ammonium nitrate is recovered via stream 16 from reactor 14.

15        The process flow sheet shown in figure 1 also includes an  $\text{NO}_3\text{-HT}$  plant 18. In order to operate this plant 18, magnesite ( $\text{MgCO}_3$ ) is reacted with nitric acid from nitric acid plant 10 in magnesite reactor 20. This converts the magnesite into magnesium nitrate, which leads magnesite reactor 20 via line 22.

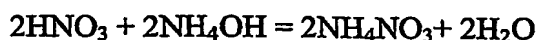
20        Sodium aluminate is supplied via line 24 into  $\text{NO}_3\text{-HT}$  plant, where it is mixed with magnesium nitrate from line 22 and ammonium hydroxide, which is supplied via line 26 from ammonia plant 12.

25        The product from the  $\text{NO}_3\text{-HT}$  plant includes  $\text{NO}_3\text{-HT}$ , ammonium nitrate and sodium nitrate. In the embodiment shown in figure 1, a mixed stream containing these components leaves  $\text{NO}_3\text{-HT}$  plant via line 28. This stream is separated into an  $\text{NO}_3\text{-HT}$  product 30. A liquid stream containing ammonium nitrate and sodium nitrate is separated from the  $\text{NO}_3\text{-HT}$  product via line 32 and is passed to crystalliser 34, where sodium nitrate 36 is crystallised out. Ammonium nitrate leaves crystalliser via line 38 and is recovered as an ammonium nitrate product.

      The overall chemical reaction for processes within the modified ammonium nitrate plant is:



If the basic reaction for ammonium nitrate manufacture is written as:



5 then 12.5 kmoles of  $\text{HNO}_3$  and 12.5 kmoles of  $\text{NH}_4\text{OH}$  are required to produce 1 tonne of ammonium nitrate.

Therefore, the additional materials required to produce 1 tonne of ammonium nitrate in the modified plant become:

- 1.25 tonne of magnesite (84%  $\text{MgCO}_3$ )
- 10 • 488 kg of aluminium trihydrate
- 1.04 tonne of solid caustic soda
- 12.5 kmoles of nitric acid

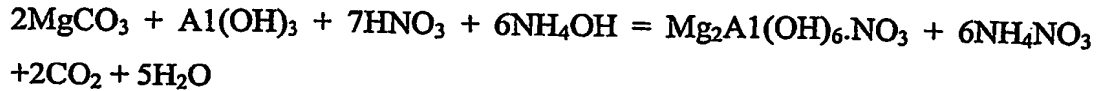
resulting in production of 1.5 tonne of  $\text{NO}_3\text{-HT}$ , along with 530kg of by-product  $\text{NaNO}_3$ .

15 Figure 2 shows a schematic process flow sheet for the synthesis of  $\text{NO}_3\text{-HT}$  using aluminium trihydrate and magnesite as additional feedstock materials. In the process flow sheet of figure 2, a conventional ammonium nitrate plant is provided and this plant is denoted by the same references numerals as those used in figure 1.

The process flow sheet figure 2 also includes an  $\text{NO}_3\text{-HT}$  plant 40. Magnesite 42  
20 is mixed with nitric acid that is supplied from nitric acid plant 10 via line 44. This produces magnesium nitrate, which is fed to  $\text{NO}_3\text{-HT}$  plant via line 46. Aluminium trihydrate 48 is reacted with nitric acid from nitric acid plant via line 50. This produces aluminium nitrate, which is supplied via line 52 to  $\text{NO}_3\text{-HT}$  plant.

Ammonium hydroxide is supplied from ammonia plant 12 via line 54 to the  $\text{NO}_3\text{-}$   
25 HT plant 40. The reaction inside  $\text{NO}_3\text{-HT}$  plant 40 results in the production of  $\text{NO}_3\text{-HT}$  product 56 and ammonium nitrate, which is recovered via line 58. It will be appreciated that ammonium nitrate and  $\text{NO}_3\text{-HT}$  product may be separated by one or more solid/liquid separation steps (not shown).

The overall chemical reaction for this synthesis route is:



Writing the basic reaction for ammonium nitrate manufacture as:



indicating that 12.5 kmols of  $\text{HNO}_3$  and 12.5 kmols of  $\text{NH}_4\text{OH}$  are required for the production of 1 tonne of ammonium nitrate.

The additional materials needed to manufacture 1 tonne of ammonium nitrate in the modified plant are:

- 10
- 416kg of magnesite (84%  $\text{MgCO}_3$ )
  - 162 kg of aluminium trihydrate
  - 2.08 kmols of  $\text{HNO}_3$

leading to the production of 0.5 tonnes of  $\text{NO}_3\text{-HT}$ .

15 Decisions relating to which synthesis pathway to follow would be based on a range of criteria including:

- the balance between  $\text{NO}_3\text{-HT}$  and ammonium nitrate required
- the relative costs of digestion of aluminium trihydrate in nitric acid and caustic soda
- the value of sodium nitrate residue vis a vis crystallisation costs
- 20 • the relative values of ammonium nitrate and sodium nitrate

Subsequent to the production of  $\text{NO}_3\text{-HT}$ , ammonium nitrate plant resources can be further used to produce  $\text{PO}_4\text{-HT}$  and  $\text{SO}_4\text{-HT}$  by introduction of phosphoric and sulphuric acids to react with plant ammonia to form solutions of ammonium phosphate and ammonium sulphate. These latter solutions would then be used to exchange nitrate in

25  $\text{NO}_3\text{-HT}$  with  $\text{PO}_4$  and  $\text{SO}_4$ , with the only residue, ammonium nitrate, being returned to the primary production stream.

Figure 3 shows possible modifications to the flow sheet shown in figure 2 in order to produce  $\text{PO}_4\text{-HT}$  product and  $\text{SO}_4\text{-HT}$  product. Where the features of figure 3 are identical to those of figure 2, they are given the same reference numerals as used in figure 2. The process flow sheet of figure 3 further includes mixing sulphuric acid 60 with ammonium to form ammonium sulphate 62. This is then ion exchanged with the  $\text{NO}_3\text{-HT}$  product to form  $\text{SO}_4\text{-HT}$  product 64 and ammonium nitrate 66. Similarly, phosphoric acid 68 can be mixed with ammonia from ammonium plant 12 to form a solution of ammonium phosphate 70. This solution is then used to ion exchange the  $\text{SO}_3\text{-HT}$  product to form  $\text{SO}_4\text{-HT}$  product 72 and ammonium nitrate 74.

Examples of the above described processes are as follows:

#### Example 1

250mL of 1.5M  $\text{Mg}(\text{NO}_3)_2$  solution obtained from the digestion of magnesite with nitric acid where combined with 250 mL of 0.75M  $\text{NaAl}(\text{OH})_4$  (diluted commercial sodium aluminate) over a 30 minute period using peristaltic pumps. The pH was maintained at 9.5-9.6 by dropwise additional of conc. aqueous ammonia. The resulting slurry was aged at  $80^\circ\text{C}$  for 8 hours, cooled, and washed with water to remove the bulk of free ammonium and sodium nitrates. The filter cake was dried at  $80^\circ\text{C}$  to yield about 50g of  $\text{NO}_3\text{-HT}$  containing 280 me/100g of exchangeable nitrate and 50 me/100g of soluble nitrate.

#### Example 2

250 mL of 2.85M  $\text{Mg}(\text{NO}_3)_2$  solution obtained from digestion of magnesite in nitric acid was combined with 250 mL of 1.425M  $\text{Al}(\text{NO}_3)_3$  solution from digestion of aluminium trihydrate in nitric acid over a 30 minute period using peristaltic pumps. The pH was maintained at 9.5-9.6 by dropwise additional of conc. aqueous ammonia. The resulting slurry was heated to  $80^\circ\text{C}$  for 8 hours, cooled, and washed with water. This product contained 265 me/100g of exchangeable nitrate and 54 me/100g of water soluble nitrate.

Examples 3 and 4 demonstrate the ion exchange of nitrate interlayer anions with phosphate and sulphate ions, respectively.

### Example 3

Ten mL of 0.25M di-ammonium phosphate solution was added to 6.2g of freshly prepared  $\text{NO}_3$ -HT filter cake (72% w/w moisture content) and intermittently agitated on a vortex stirrer over a one hour period. After centrifugation, the concentrations of phosphate and nitrate in the supernatant solution were 14 ppm P and 4370 ppm N, demonstrating effective replacement of nitrate in the HT by phosphate.

### Example 4

Ten mL of 0.25M ammonium sulphate solution was added to 8.8 of freshly prepared  $\text{NO}_3$ -HT filter cake (72% w/w moisture content) and intermittently agitated on a vortex stirrer over a one hour period. After configuration, the concentrations of sulphate and nitrate in the supernatant solution were 20 ppm S and 3910 ppm N, demonstrating effective replacement of nitrate in the HT by sulphate.

Figures 4, 5 and 6 show alternative embodiments of the present invention that involve at least partial recycle of ammonium nitrate produced in step (6).

Figure 4 shows a schematic process flow chart that incorporates the production of  $\text{NO}_3$ -HT into an ammonium nitrate plant. Nitric acid from a nitric acid plant 10 and ammonia from an ammonia plant 12 are mixed and reacted in reactor 14 to produce ammonium nitrate. Ammonium nitrate is recovered via stream 16 from reactor 14.

The process flow sheet shown in Figure 4 also includes a  $\text{NO}_3$ -HT plant 18. In order to operate this plant 18, calcined magnesite ( $\text{MgO}$ ) is reacted with ammonium nitrate (initially accumulated in ammonium nitrate accumulator 20) in magnesium oxide reactor 22. This converts the magnesium oxide to magnesium nitrate and ammonia. The ammonia is returned to the ammonia plant 12 via line 24. A portion of magnesium nitrate from the magnesium oxide reactor 22 is sent to the  $\text{NO}_3$ -HT plant via line 26, the remainder being accumulated in magnesium nitrate accumulator 28.

Aluminium trihydrate 30 is reacted with nitric acid from the nitric acid plant 10 supplied via line 32, to produce aluminium nitrate. The aluminium nitrate is sent to the  $\text{NO}_3$ -HT plant 18 through line 33. Ammonia from the ammonia plant 12 is supplied to the  $\text{NO}_3$ -HT plant 18 via line 34. The reaction inside the  $\text{NO}_3$ -HT plant 18 results in the



production of  $\text{NO}_3\text{-HT}$  product 36, which is recovered via line 38, and of ammonium nitrate which is sent to the ammonium nitrate accumulator 20. It will be appreciated that ammonium nitrate and  $\text{NO}_3\text{-HT}$  product may be separated by one or more solid/liquid separation steps (not shown).

5           Figure 5 schematically illustrates Phase 2 of the process whereby the magnesium oxide reactor (22 in Figure 1) is stopped while magnesium nitrate is supplied to the  $\text{NO}_3\text{-HT}$  plant 18 from the magnesium nitrate accumulator 28 via line 40. Aluminium nitrate and ammonia are supplied to the  $\text{NO}_3\text{-HT}$  plant 18 as previously described, and ammonium nitrate from the  $\text{NO}_3\text{-HT}$  plant 18 is allowed to accumulate in the ammonium nitrate accumulator 20. When the magnesium nitrate supply from the magnesium nitrate accumulator 28 is exhausted, the process reverts to Phase 1.

10           Figure 6 schematically illustrates that portion of the process whereby  $\text{NO}_3\text{-HT}$  product 18 can be reacted with ammonium sulphate and ammonium phosphate to form  $\text{SO}_4\text{-HT}$  42 and  $\text{PO}_4\text{-HT}$  44 respectively, with the residual ammonium nitrate returned via line 46 to the ammonium nitrate accumulator 20. The ammonium sulphate and ammonium phosphate reactants can be synthesised on site by reacting sulphuric acid and phosphoric acid with ammonia from the ammonia plant 12. It is further shown that an LDH material containing  $\text{CO}_3$  in the interlayers ( $\text{CO}_3\text{-HT}$ ) can be produced from  $\text{NO}_3\text{-HT}$  product 48 by bubbling  $\text{CO}_2$  through the  $\text{NO}_3\text{-HT}$  slurry. Though of limited agricultural use,  $\text{CO}_3\text{-HT}$  is used in a wide range of industrial applications.

15           Figure 7 shows a flowsheet of another embodiment of the present invention. In the process of Figure 7, step (4) of the process (as described on pages 5 and 4 of this specification) forms a nitrate of the first metal by contacting a compound containing the first metal with ammonium nitrate and step (5) of the process involves the step (5)(a)(11).  
20           The flowsheet of Figure 7 shows recycle of the ammonium nitrate produced in the hydrotalcite formation step back to the steps for making magnesium nitrate and aluminium nitrate. Due to the mass balance requirements of this embodiment of the invention, all of the ammonium nitrate formed in the hydrotalcite production step can be recycled and further ammonium nitrate is also required for make-up. The recycling of the  
25           ammonium nitrate means that the process of Figure 7 does not have an ammonium nitrate  
30

product stream. Thus, the economics of the process do not require a viable market for ammonium nitrate and consequently the flowsheet of Figure 7 does not have to be tied to an ammonium nitrate plant. Further, the recycle of the ammonium nitrate formed in the hydrotalcite production step also reduces the amount of feedstock reagents required in the process.

Turning now to Figure 7, the process of Figure 7 involves providing nitric acid from a source of nitric acid 102 and ammonia from a source of ammonia 104. The source of nitric acid may be a nitric acid plant or a nitric acid storage facility. The source of ammonia may be an ammonia plant or an ammonia storage facility.

The nitric acid and ammonia are contacted under appropriate conditions in reactor 106 to produce ammonium nitrate. As an alternative, ammonium nitrate may be supplied from a separate source.

Calcined magnesia is mixed with ammonium nitrate in reactor 108 to produce magnesium nitrate and ammonia. The ammonia may be returned to ammonia source 104. The ammonium nitrate from reactor 106 is also mixed with aluminium trihydroxide in reactor 110 to form aluminium nitrate and ammonium hydroxide. The ammonium hydroxide may be returned to source ammonia 104.

Subsequently, the magnesium nitrate, aluminium nitrate and ammonium hydroxide are mixed in reactor 112 to produce hydrotalcite having nitrate as interlayer anions and ammonium nitrate. Following suitable liquid/solid separation steps, the hydrotalcite is separated from the ammonium nitrate. The hydrotalcite may be further treated, for example, as described with reference to Figure 3. The ammonium nitrate is recycled back to be mixed with further calcined magnesite and aluminium trihydroxide. Due to the mass balance requirements of the process (as outlined below), some make-up ammonium nitrate will be required, although the amount of ammonium nitrate required is significantly reduced by the recycling of ammonium nitrate.

The steps involved in this process are as follows:

- (a) produce seven moles of ammonium nitrate by reaction of ammonia and nitric acid;

(b) use four moles of ammonium nitrate to react with two moles of calcined magnesia to produce two moles of magnesium nitrate and ammonia;

(c) use three moles of ammonium nitrate to react with one mole of aluminium trihydroxide to form one mole of aluminium nitrate and ammonia;

5 (d) mix the magnesium nitrate, aluminium nitrate and appropriate amount of ammonia to form hydrotalcite having nitrate interlayer anions and six moles of ammonium nitrate;

(e) recycle the six moles of ammonium nitrate to steps (b) and (c) above; and

10 (f) produce one mole of ammonium nitrate to provide the required amounts of ammonium nitrate for steps (b) and (c).

In continuous operation, the process of Figure 7 effectively involves steps (b) to (f).

15 The process of Figure 7 requires a reduced production of ammonium nitrate due to the closed loop recycle of ammonium nitrate. The process of Figure 7 can also be stand-alone from an ammonium nitrate plant as ammonium nitrate is not a product of the process. It is, of course, possible that the process of Figure 7 could also be integrated into an ammonium nitrate plant.

20 Those skilled in the art will appreciate that the invention described herein may be susceptible to variations and modifications other than those specifically described. It will be understood that the present invention encompasses all such variations and modifications that fall within its spirit and scope.

**Dated this 15th day of April, 2003**

**Commonwealth Scientific and Industrial Research Organisation**

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**by its attorneys**

**Freehills Carter Smith Beadle**

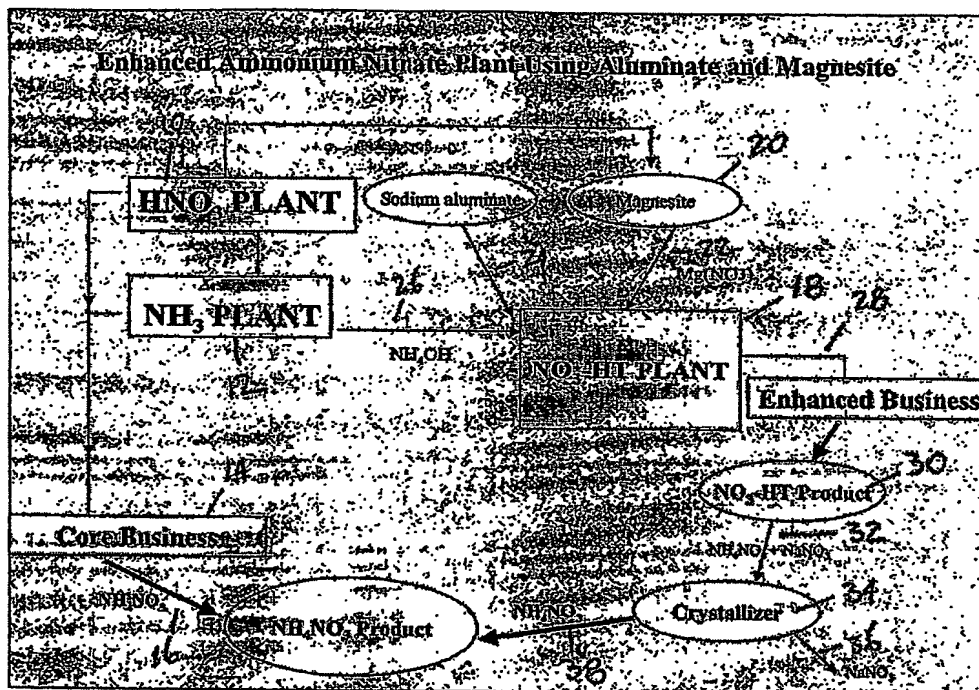


FIGURE 1.

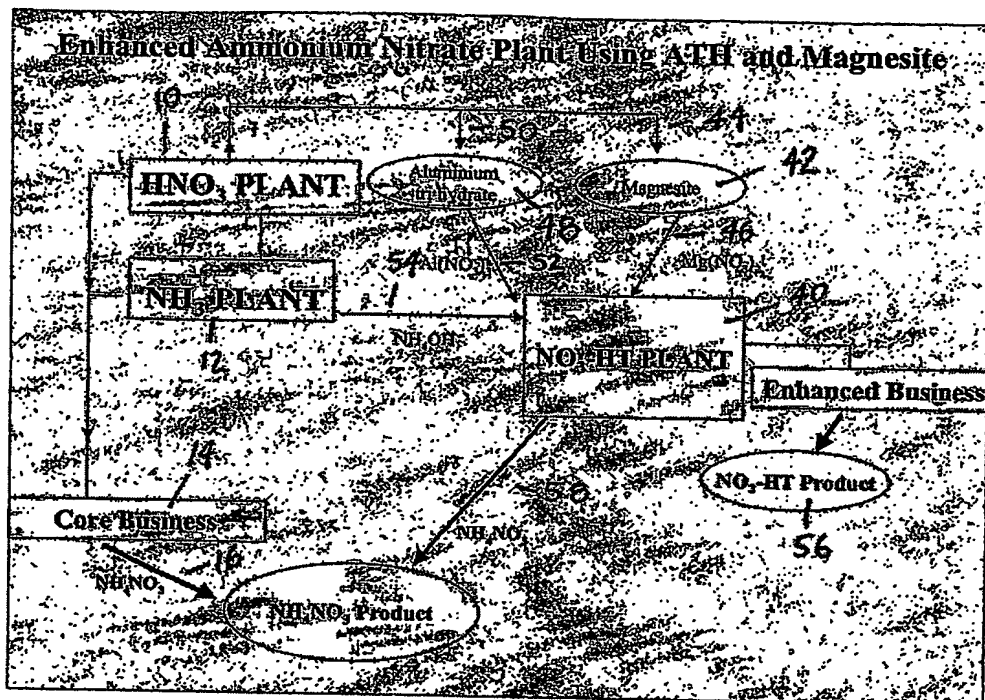


FIGURE 2.

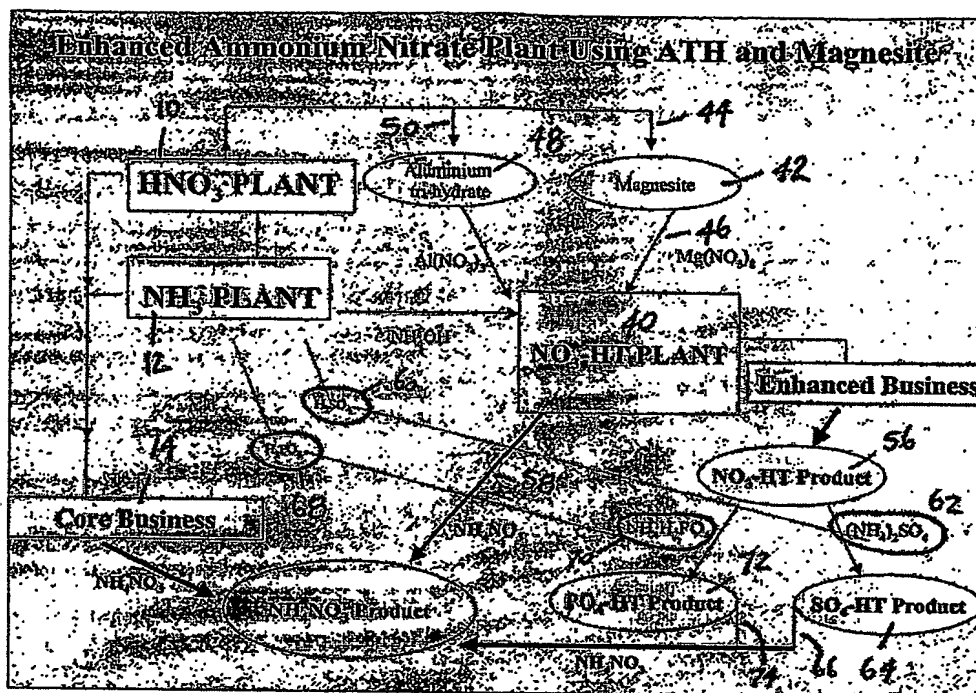


FIGURE 3

# Enhanced Ammonium Nitrate Plant Using ATH and Magnesite

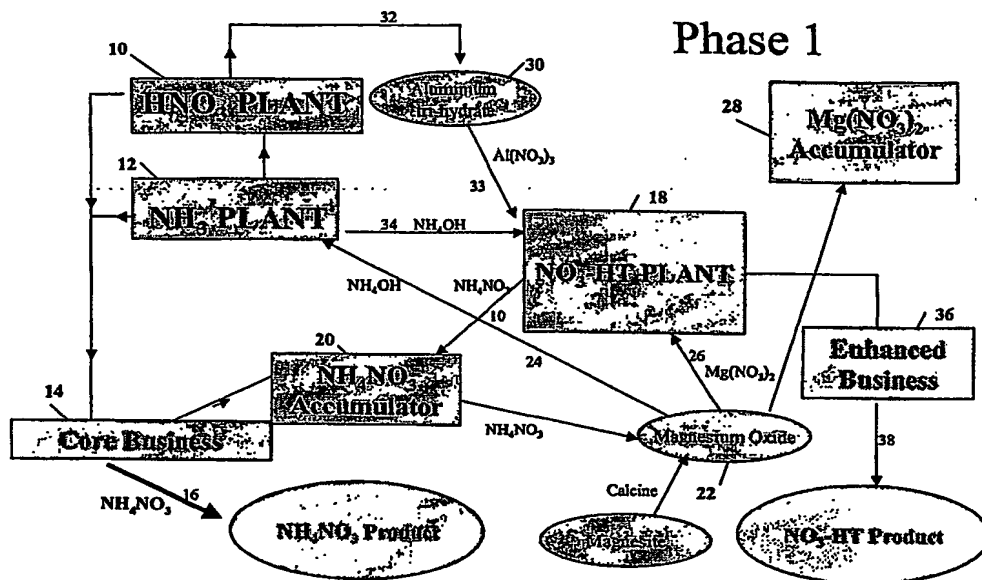


Figure 4.

# Enhanced Ammonium Nitrate Plant Using ATH and Magnesite

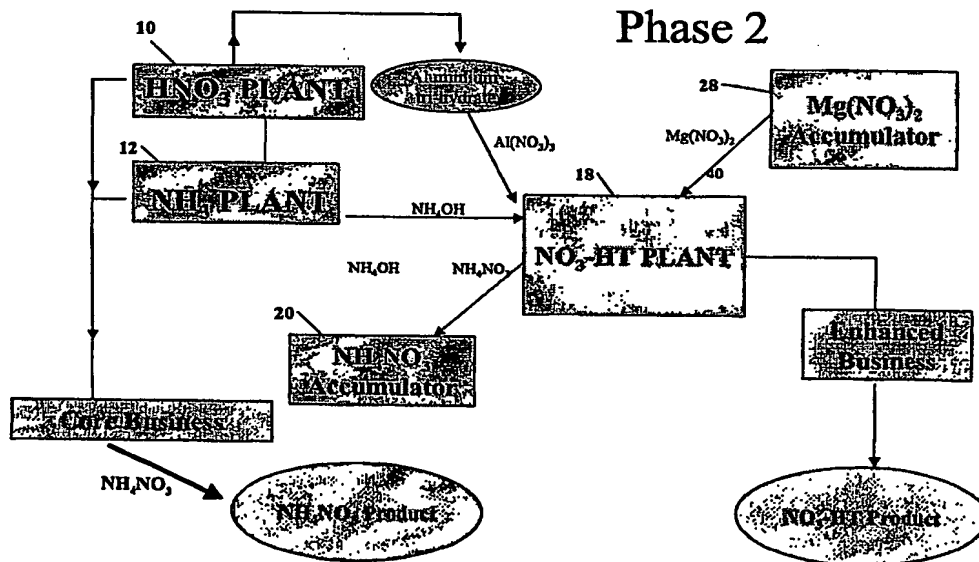


Figure 5

# Enhanced Ammonium Nitrate Plant Using ATH and Magnesite

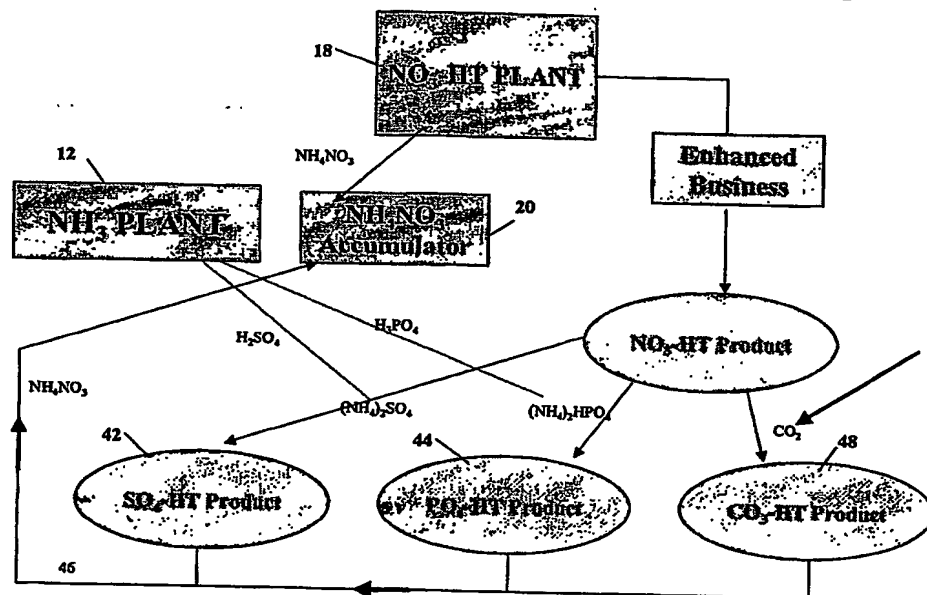


Figure 6



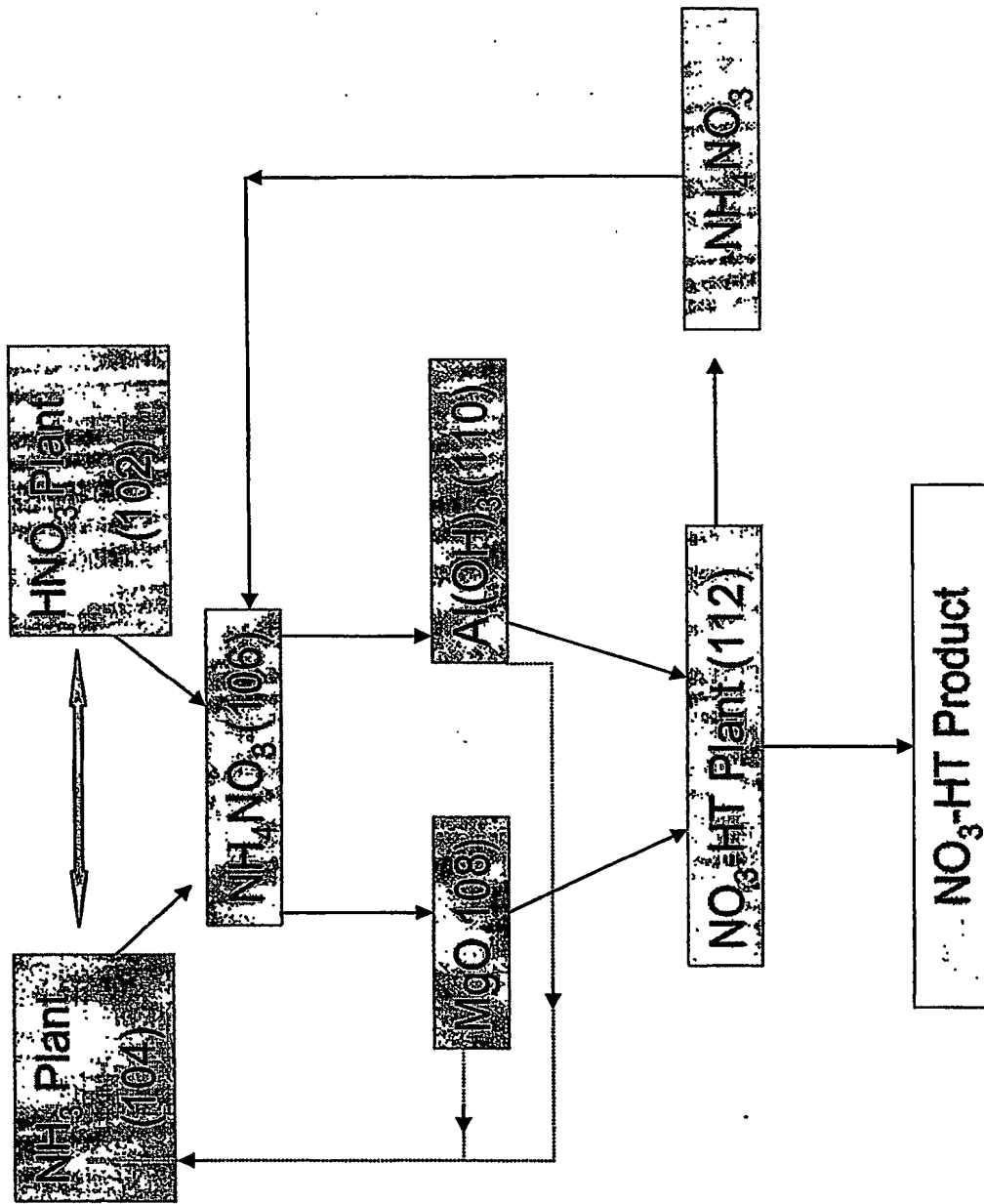


Figure 7

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